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Carbohydrates

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The term "carbohydrates" des ibes a major group of naturally occurring c mical compounds of widely varying molec r mass. The low molecular mass carbohydra comprise a family of more or less sweet- ting, water-soluble, colorless products with osely related physical, chemical, and physiolog l properties. They are often generically calle "sugars," reflecting their relationship to "su r," which is the familiar sucrose.

The high molecular mass car hydrates are called *polysaccharides*. Their phy al properties differ significantly from those of w molecular mass. They do not taste sweet ar many do not dissolve in water.

All carbohydrates are comp d of units of *monosaccharides* or their deriva es. Carbohydrates are usually classified by e number of monosaccharide units in their molecules. A monosaccharide contains an uninterrupted chain of a limited number (five a d six are most common) of carbon atoms. In c gosaccharides (disaccharide, trisaccharide, trasaccharide, etc.) and in polysaccharides, n nosaccharides are linked together through gl osidic oxygen atoms.

Oligosaccharides are consid ed to be low molecular mass carbohydrates. ere is, however, no definite borderline betw the oligosaccharides and the polysacchari s. In general, naturally occurring oligosaccha les rarely consist of more than 5, and polysaccharides of less than 100, monosaccharide units.

Most monosaccharides, oligosaccharides, and polysaccharides have the common molecular formula $C_n(H_2O)_m$ (from which the common name "carbohydrates" is derived), in which n is either equal to m (monosaccharides) or a little larger than m (oligo- and polysaccharides). Oligomers are formed by condensation (formal elimination of water) of monosaccharide units, and conversely oligo- and polysaccharides can be degraded to monosaccharides by hydrolysis. The whole biomass on earth has been estimated to be about 90% carbohydrates, which means that the molecular formula of the total organic matter on earth is only slightly different from that of the carbohydrates.

Carbohydrates have important functions: primarily they supply chemical energy to the living cell and serve as raw materials for the construction of other natural products. Carbohydrates are mainly formed in the photochemical carbon dioxide fixation in green plants, a complicated biochemical process which provides for the efficient conversion of solar energy into chemical energy. The use of carbohydrates for the supply of primary energy and as raw materials in synthetic organic chemistry represent an important facet of present and future technology.

Carbohydrates are industrially utilized to a considerable extent. Glucose [50-99-7] is the

starting material for the produ on of vitamin C (ascorbic acid). Maltose [69-7 6], a product of the enzymatic degradation of arch, can be reduced to maltitol, which is use as a low-calorie sweetener. A similar sweetener isomalt (palatinit) [64519-82-0], a mixture o the disaccharide alcohols O-α-D-glucopyrano -(1 → 1)-D-mannitol [20942-99-8] and O-α- glucopyranosyl-(1 → 6)-D-glucitol [534-73-6], which are obtained by reduction of isomal tose (palatinose) [13718-94-0], a product of en matic isomerization of sucrose. Fructose [57-4 7] itself is used as a sweetener by diabetics.

Many nonionic detergent are derived from carbohydrates. Used in soap shampoo, they are less irritating than their nic counterparts and can easily be degraded logically, therefore causing no environmen problem. Polysaccharides are produced and sed in a wide variety of applications. These lude substitutes for blood serum (dextran), rivatives (cellulose and starch basis), wrappin material (cellophane), additives to food an beverages, pharmaceuticals and cosmetics (arch, pectic substances, plant and microbial ms), and drilling fluids in oil fields. Cellulose i he form of wood or cotton is one of the most i portant industrial raw materials.

Production. Natural carb hydrates are obtained exclusively from biolo al sources. Total syntheses are impractical, a even the simple 3-epimerization of D-glucose to another monosaccharide, D-allose, which not found in nature, is tedious. Chemical ntheses of oligosaccharides by coupling suit ble derivatives of monosaccharides are extre ly difficult and only possible on a small scale The chemical synthesis of a polysaccharide is most impossible. One possibility is the poly erization of 1,6-anhydro sugar derivatives, ch as substituted levoglucosans, which yields 1 → 6)-α-D-glucopyranans.

1. Monosaccharides

Monosaccharides are eit r polyhydroxy aldehydes (-oses, aldoses) or p yhydroxy ketones (-uloses, ketoses). The carb skeleton in most monosaccharides is linear (n branched). In almost all ketoses the carbony roup is located at carbon atom 2. Most mono charides have either six (hexoses and hexulo) or five (pentoses and pentuloses) carbon atoms. Monosaccharides with fewer carbon atoms (trioses, tetroses, and tetruloses) or more carbon atoms (heptoses, octoses, heptuloses, octuloses, etc.) rare. The most important and abundant monosaccharides are hexoses: D-glucose, D-mannose, and D-galactose. D-Fructose is a hexulose. Ubiquitous pentoses are L-arabinose, D-xylose, and D-ribose.

Stereoisomerism. Monosaccharides (as polyhydroxy aldehydes or ketones) possess several asymmetric carbon atoms. Hexoses have four, hexuloses and pentoses three, and pentuloses two chirality centers. The existence of several asymmetric carbon atoms in one molecule gives rise to families of stereoisomers. For a hexose with four asymmetric carbon atoms, there exist 2^4 stereoisomers, eight of which are enantiomers (mirror images) of the other eight. Hexuloses exist in four pairs of enantiomers, pentuloses and tetroses in two. The diastereomeric monosaccharides (diastereomers are stereoisomers that are not mirror images of each other) have trivial names. In Figure 1, D-hexoses, D-hexuloses, D-pentoses, and D-tetroses are represented as open-chain Fischer projections. In the Fischer projection all carbon atoms form a bow with the convex part pointing toward the viewer. According to the Fischer convention, the orientation of the hydroxyl group attached to the highest numbered asymmetric carbon atom determines whether a monosaccharide belongs to the D- or the L-series. If this group is positioned on the right of the carbon chain, assignment is to the D-series, and vice versa. Most naturally occurring monosaccharides have the D-configuration. The chirality of carbohydrates makes this class of natural compounds an ideal source for the preparation of chiral synthons (intermediates for chemical synthesis), which are needed for the syntheses of pharmaceuticals, agrochemicals, pheromones, etc. [26], [27].

Pyranoses and Furanoses. Monosaccharides form cyclic intramolecular hemiacetals if their carbon skeleton permits. The relative stabilities of these hemiacetals depend on the ring size. In general, six-membered rings (pyranoses) are most common, whereas only a few five-membered rings (furanoses) are stable. Smaller rings are unstable, and larger ones can only be detected in aqueous equilibrium mixtures. Structures of the cyclic hemiacetals are represented by the Haworth projection formulas of the D-series

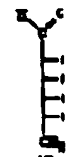

Figure 1.

Figure 2. Vertical

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Cellulose

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1. Cellulose

Cellulose [9004-34-6] deserve a special position among the industrially use raw materials for two general reasons. First, c ulose belongs to the natural products which, v en used carefully, are inexhaustible since it is gularly regenerated by nature in relatively sho time periods. As long as we ensure that the pri ary sources of cellulose, forests and cotton plan tions, are not damaged by destructive lumberi or overcropping, we can expect regular and s nificant natural annual reproduction.

According to reference [8], tl annual yield of cellulosic matter resulting from hotoinitiated biosynthesis amounts to approximately 1.3×10^{9} metric tons. A tree produces an average of 13.7 g of cellulose daily. If they were lined up, the cellulose chain molecules formed each day would result in a string of 2.62×10^{10} km in length, or 175 times the distance between the sun and the earth.

In wood, cellulose is part of an ingeniously constructed fiber-reinforced composite in which long, stiff cellulose chain molecules organized in thin fibrils constitute the plant reticulum material held together and protected by hydrophobic lignin acting as binder and encasement.

To isolate cellulose from wood for industrial applications, the wooden composite must be broken up by so-called pulping processes. In

these treatments, other wo l constituents, such as lignin and hemicellulose are to a large extent degraded and dissolved. T s far, these byproducts have found only limit use. In most cases, wood pulp manufacturers concentrate the waste pulping liquors to concent tes consisting of ca. 50% solids. The organic n tter is used as fuel to produce steam and electric ower, while the inorganic pulping chemicals da, magnesium, or ammonium base and sulfi dioxide) are simultaneously recovered. The recovery processes have practically solved t long-standing environmental problems of th wood pulp industry.

Both cellulose and lig are biologically degradable and, thus, ecolo ally beneficial. They will decompose in the op . Cellulose products, such as paper or cellulo textiles, will decompose and eventually form aluable humus. In industrial use, environme al problems are not caused by cellulose or lig but by the chemicals used in the isolation or subsequent chemical processing and transfo ation into cellulose derivatives, films, or fibe . Therefore, the long-term task of modern cell se research will be the development of novel p cesses which yield no or only a few ecological armful byproducts. If these efforts are succes l, cellulose will surely maintain and strengthe s position as a renewable and environmental beneficial, industrially important raw material mpeting with synthetically produced polymer

1.1. Properties

1.1.1. Molecular Stru re

Cellulose is an iso tic β-1,4-polyacetal of cellobiose (4-*O*-β-D-gl opyranosyl-D-glucose). The actual base unit, t cellobiose, consists of two molecules of gluco . For this reason, cellulose can also be consi red as a (syndiotactic) polyacetal of glucose.

Basic Structure. T basic chemical formula of cellulose is the follo ing:

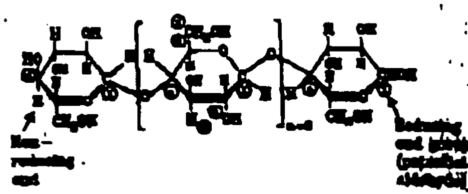
$C_6H_{10n-}{}_2O_{5n+1} = (C_6H_{10}O$ or $(C_6H_{10}O_5)_n$

where P = the degree of p merization; n = the number of units in the chain.

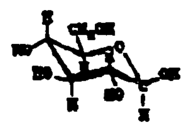
The elemental co position of 44.4% C, 6.2% H, and 49.4% was already known to PAYEN in 1842 [9]. T molecular mass of the glucose base unit is $m_0 = 162$, and the molecular mass of the cellulose polymer is

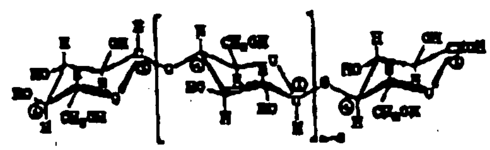
$M_r = m_0 P + 18 \approx 162\,P.$

Constitutional Formula. HAWORTH [10] first discovered the covalent bonds inside and between the glucose units while STAUDINGER [11] found the final proof for the macromolecular nature of the cellulose molecule.



Conformational Formula. The glucopyranosic ring adopts a $^4C_1$ chair conformation, as revealed by recent X-ray crystallography and nuclear magnetic resonance studies [12], [13] with glucose. The chair formation in comparison to the tray conformation exhibits a free stabilization enthalpy of $G_s = 20.05$ kJ/mol [14]. In this conformation, the three hydroxyl groups are positioned in the ring plane while the hydrogen atoms are in a vertical position. It seems only natural to assume that the same conformation also exists in the cellulose molecule.





Structural Anomalies. As a naturally occurring polymer, cellulose always contains small amounts of other constituents in addition to glucose (over 99%). These may already be partially built into or onto the cellulose molecules during biosynthesis, such as lignin–cellulose complexes [15]. Most of the changes in the molecular structure, however, result from secondary reactions, i.e., hydrolysis or oxidation, during isolation from natural sources. For morphological reasons, such chemical changes occur preferably in

the accessible interlinking regi s between the crystallites of the elementary fi ils or their aggregations. The glucosidic link s these accessible areas, especially if oxidized s are also present, split 1000–5000 times fast than glucosidic linkages inside the well-orderec rystallites. The existence of weak links, as prop ed in reference [16], is hard to determine. In h ogeneous acid hydrolysis, all glucosidic link s split at the same rate [17].

Cellulose always contains c rboxyl groups: In wood pulp, one –COOH gro per 100–1000 anhydroglucose units (AHG) ists; in cotton, one –COOH group per 100–X AHG units.

Molecular Size. The molecul size of a polymer can be defined by its averag olecular mass ($\bar{M}_r$) or its average degree of pol merization ($\bar{P}$): whereby $\bar{M}_r = \bar{P} m_0$ (m_0 = mole lar mass of the base unit, i.e., of glucose in the c e of cellulose).

By investigation of certain ysical properties of cellulose or polyhomolog s cellulose derivative solutions, the averag gree of polymerization can be determined. ble 1 lists the number average degree of poly erization of a number of celluloses of various rigin.

For such physical investig ons, cellulose solutions in aqueous copper(II strammonium hydroxide (Schweizer's reagent: Cuoxam), copper(II)ethylenediamine hydrox (Cuen), alkaline solutions of the ethyler liamine complexes of cadmium or nickel an be used. Cellulose trinitrate (CTN) or ce lose tricarbanilate (CTC) solutions in appr riate solvents are also suitable for such studies e Table 2). In the latter, it should be kept in nd that chain degradation often occurs in su titution reactions performed under unfavora e conditions.

Table 1. Degree of polymerization of ce loses of different origin [18]

Type of cellulose	$\bar{P}_n$
Cotton, raw	7 000
Cotton, raw (according to Russian wor	14 000
Cotton, purified	1 500–300
Cotton linters	6 500
Flax	8 000
Ramie	6 500
α-Cellulose (isolated from wood fibers)	1 100–800
Spruce, pulped	3 300
Beech, pulped	3 050
Aspen	2 500
Fir	2 500
Bacterial cellulose	2 700
Acetobacter cellulose	600

Light scattering studies performed on dilute solutions of cellulose or cellulose derivatives will yield the weight average ($\bar{M}_w$) and osmotic measurements the number average ($\bar{M}_n$) of the molecular mass (or the corresponding average degrees of polymerization: $\bar{P}_w$ or $\bar{P}_n$). Sedimentation experiments in an ultracentrifuge enable the determination of a higher order average molecular mass, the so-called "Z-average" ($\bar{M}_z$). These various quantities are defined as follows:

$$\bar{M}_n = \frac{\sum N_i \cdot M_i}{\sum N_i} \quad \text{or} \quad \bar{P}_n = \frac{\sum N_i \cdot P_i}{\sum N_i} \quad \text{(weight average)}$$

$$\bar{M}_w = \frac{\sum N_i \cdot M_i^2}{\sum N_i \cdot M_i} \quad \text{or} \quad \bar{P}_w = \frac{\sum N_i \cdot P_i^2}{\sum N_i \cdot P_i} \quad \text{(number average)}$$

$$\bar{M}_z = \frac{\sum N_i \cdot M_i^3}{\sum N_i \cdot M_i^2} \quad \text{or} \quad \bar{P}_z = \frac{\sum N_i \cdot P_i^3}{\sum N_i \cdot P_i^2} \quad \text{(Z-average).}$$

whereby $M = 162 P_i$; i = fraction 1, 2, 3 … i; N = number of molecules with $M_1, M_2 \dots M_i$ or $P_1, P_2 \dots P_i$.

The simplest and most widely applied practical method for the determination of the degree of polymerization is based on measuring the "intrinsic viscosity η" (Staudinger index). The intrinsic viscosity expresses the reduced viscosity of a solution at an infinitely small concentration. The latter can be derived from the relative viscosity, which is the ratio of the flow time of the dilute polymer solution of a given concentration (t_{sol}) and that of the solvent (t_s) in a capillary viscometer:

$$\eta_{rel} = t_{sol}/t_s$$

$$\eta_{red} = \frac{\eta_{rel} - 1}{c}$$

wherein c = concentration of the cellulose or its derivative in the solution.

The degree of polymerization can be calculated from [η] by using the formula:

$$[\eta] = \lim_{c \to 0} \eta_{red} = K_\eta \bar{P}_v^a \quad (\text{or} \quad K_m M_r^a)$$

The definition of $\bar{P}_v$ (viscosity average of the degree of polymerization) is as follows:

$$\bar{P}_v = \left\{ \frac{w_i P_i^{(1+a)}}{w_i P_i} \right\}^{1/a}$$

wherein w_i = weight fraction of a molecularly uniform fraction with a degree of polymerization of P_i; $\bar{P}_v$ = viscosity average of the degree of polymerization which for cellulose or cellulose derivative solutions closely resembles the weight average $\bar{P}_w$; and $\bar{M}_v$ = viscosity average of the molecular mass.